# Armed Services Technical Information Agency

**AD 41051**

THE REACTIONS OF FREE RADICALS IN SOLUTION

A TECHNICAL PROGRESS REPORT

ONR CONTRACT

Iowa State College

George S. Hammond, Jyotirindra N. Sen,
George B. Lucas and John Tanaka

During the period from March 15, 1951 to the present time
work under this project has been conducted with three general
objectives. The first is the investigation of the reactions
of the primary products of thermal decomposition reactions in
order to help establish generalizations concerning relative
reactivity and mechanism in free radical reactions. The second,
while novel and highly interesting in its own right, is actually
a necessary step in the interpretation of our results in terms
of our first objective. This is the study of effects which are
unique to thermal decomposition in that they are due to the
occurrence of diffusion controlled reactions of two primary
decomposition products with each other. The last objective has
been the study of the reactions of triphenylmethyl with various
organic compounds in the hope that information could be obtained
which would shed light on the behavior of more reactive radicals.

Progress toward the first two objectives may be considered
normal and gratifying. The third line of endeavor has been
disappointing in that a great deal of time has been expended
in a reinvestigation of the behavior of triphenylmethyl in the
presence of nitrobenzene. Results which were reported earlier

by Dr. Raave have been impossible to repeat with the result
that implications of considerable significance which had pre-
viously been drawn must now be considered to be unfounded.

It is hoped that the work can be continued and a proposal
has been submitted to the National Science Foundation with the
hope that that agency will be able to support a continuation
of these studies.  The generous support of the Office of Naval
Research has been much appreciated.  Without such support much
of our work would have been impossible.  Three post-doctoral
fellows have been employed on the project.  They are Dr. Louis
Soffer, now senior chemist at Aberdeen Proving Ground, Dr. Raave
whose present connection is unknown, and Dr. Jyotirindra N. Sen
who is on leave of absence from the Calcutta Institute for the
Advancement of Science.  One graduate student, Dr. George B.
Lucas, has completed a doctoral dissertation from his studies
and has been granted his Ph.D. degree.  He is at present a
senior chemist with the Redstone Arsenal Research Division of
the Rohm and Haas Company.  A second student, Mr. John Tanaka,
has made a substantial start on his doctoral research under
the contract.  In addition, Dr. Charles E. Boozer who has been
employed under another grant has contributed to the work by
supplying data on the rate of decomposition of azo-bis-isobutyro-
nitrile in various solvents and by helpful consultation.

Part of the work is reported and discussed in a copy of a
long abstract which has been accepted by the Physical and

Inorganic Division of the American Chemical Society for presentation at the Kansas City Meeting in March. This paper is, in essence, a first draft of a manuscript which we hope to submit for publication in the near future. Manuscripts are also in preparation which will report the studies of the polymerization of methacrylonitrile and of the decomposition of azonitriles in the presence of chloranil. Publication on the latter subject is to be delayed, however, as Dr. Lucas is currently checking related results recently reported by other workers which are surprising in the light of our observations. Other work must be further elaborated before it is suitable for publication.

## Experimental

Toluene (Baker and Adamson, Reagent Grade) was distilled through a six-foot column packed with glass helices. The fraction boiling at 109-110° (uncorr.) was used in subsequent work.

Cumene (Eastman Kodak White Label) was distilled using a Vigreux still head. The liquid boiling at 151.5-152°(uncorr.) was stored over calcium metal chips and used throughout.

Tetralin (Eastman Kodak White Label) was distilled at 91°/18 mm. through a six-foot helix packed column.

Chlorobenzene (Paragon Division, Matheson Chemical Co.) was used without further purification.

Chloranil (Eastman Kodak Yellow Label) was recrystallized from glacial acetic acid and dried over sodium hydroxide in a vacuum desiccator.

**Azo-bis-diethylacetonitrile** was prepared by the method of Dox(1). The yield was 60 per cent, m.p. after two

(1). A. Dox, J. Am. Chem. Soc., 47, 1473 (1925).

recrystallizations from ethanol, 74-5°.

**Azo-bis-isobutyronitrile** was prepared by the method of Dox (1) in 70 per cent yield. After two recrystallizations the product melted at 101-2°.

**$\omega$, $\omega'$-Azo-bis-toluene** - was prepared by the method of Bickel and Waters (2). The product was never obtained in a high state

(2) Bickel and W. A. Waters, Rec. Trav. Chim, 69, 312 (1950).

of purity but seemed to be contaminated by a high melting by-product ($\sim$127-30°) which was believed to be benzalbenzyl-hydrazone. However, after a number of recrystallizations from 95 per cent ethanol in a dry ice-acetone bath, a product melting at 31-3° [lit. (2)] was obtained.

**Di-t-butyl peroxide**, donated by the Shell Development Corporation, Emeryville, California, was distilled through a 44 plate glass center-rod column (45°/20 mm.) before use.

**Cumene hydroperoxide** (79 per cent in cumene) donated by the Hercules Powder Company was purified by first precipitating the sodium salt by shaking with 50 per cent aqueous sodium hydroxide and neutralizing exactly with 2N sulfuric acid (3). After

(3) Hock and Lang, Ber., 77, 257 (1944).

washing with potassium carbonate solution to insure complete
removal of acid, the material was distilled at 41°/0.01 mm.
The product gave 98 per cent of the theoretical iodometric titer.

Cumyl alcohol was prepared by the method of Kharasch et. al. (4)

(4)  M. S. Kharasch, Fono and Nudenberg, J. Org. Chem., 16, 113, (1951).

from cumene hydroperoxide.  The product, after distillation
through the center-rod column and three recrystallizations from
petroleum ether, melted at 36-36.5°.

Di-𝛼- cumyl peroxide was prepared by thermal decomposition
of cumene hydroperoxide in 𝛼-cumyl alcohol at 95° (5).  Although

(5)  M. S. Kharasch, Fono and Nudenberg, ibid. 15, 753 (1950).

it is reported that near quantitative yields can be obtained
we were able to obtain only 5-10 per cent.  After recrystalli-
zation from ethanol in a dry-ice-acetone bath the product
melted at 39.0-39.5°.

t-Butyl hydroperoxide was prepared by the method of Milas
and Surgenor (6).  It was separated from the dialkyl peroxide

(6)  Milas and Surgenor, J. Am. Chem. Soc., 68, 207 (1946).

by precipitation of the sodium salt and neutralization with
2N sulfuric acid.

Decomposition of Azo-bis-diethylacetonitrile in Toluene.
Three and three tenths g. (0.015 mole) azo-nitrile was dissolved
in 50 ml. toluene and the solution was refluxed for 15 hours.
The toluene was then stripped under reduced pressure at head

temperatures below 0°. After 3-4 hours at room temperature
the residue deposited crystals of tetraethylsuccinonitrile.
The distillation of toluene was then resumed and after the
removal of a small amount a second crop of dinitrile was obtained.
The total yield was 2.09 g. (73 per cent) which melted at 47-48°
after recrystallization from ethanol-water. Neither the dis-
tillate nor recrystallization residues appeared to contain
sym-diphenylethane.

Decomposition of Azo-bis-diethylacetonitrile in Toluene
containing Chloranil. Two and two tenths g. (0.010 moles)
of Azo-bis-diethylacetonitrile and 2.48 g. (0.010 g.) chloranil
were dissolved in 100 ml. toluene and heated at reflux for 15
hours. The solution was then cooled and extracted with five
per cent aqueous sodium hydroxide until the extract was color-
less. The extract was deep red in color due to the formation
of chloranilic acid. Upon acidification with five per cent
hydrochloric acid a dirty brown solid was precipitated. After
repeated recrystallization from glacial acetic acid this pro-
duct gave white crystals of tetrachlorohydroquinone monobenzyl
ether. The yield was 0.53 g. (16 per cent). Anal. calc. for
$C_{13}H_8O_2Cl_4$: C, 46.3; H, 2.47; Cl, 42.1; found; C, 46.6; H, 2.48;
Cl, 41.6 (7).

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(7)  All analyses by Drs. Weiler and Straus, Microanalytical
     Laboratory, Oxford, England.

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The organic layer from the extraction was steam distilled
and the distillate which contained all of the toluene was

extracted with ether and the extract was dried over anhydrous sodium sulfate. After drying, the toluene-ether mixture was distilled under reduced pressure as in the previous experiment. The residue, worked up as in the control, gave 0.6 g. (31 per cent) tetraethylsuccinonitrile.

The residue from the steam distillation was recrystallized from a large volume of ethanol and gave 1.55 g. (45 per cent based on azonitrile) tetrachlorohydroquinone di-(3-cyano-3-pentyl) ether, m.p. 166-7°. Anal. calc. for $C_{18}H_{20}O_2N_2Cl_4$; C, 49.3; H, 4.56; Cl, 32.4; N, 6.39; found C, 50.1; H, 4.42; Cl, 31.7; N, 6.32.

Decomposition of Azo-bis-diethylacetonitrile in Chlorobenzene Containing Chloranil. The reaction was carried out and products were isolated by a procedure essentially identical with that described above for the experiment in toluene. The phenolic product obtained was not identical with that obtained in toluene solution and, on the basis of elementary analysis, was assigned the structure tetrachlorohydroquinone mono(3-cyano-3-pentyl) ether, m.p. 165°. Anal. calc. for $C_{12}H_{11}O_2NCl_4$; N, 4.08; Cl. 41.4; found; N, 4.17; Cl, 40.7.

Yields and material balance are included in Table I.

Decomposition of Azo-bis-isobutyronitrile in toluene containing Chloranil. The decomposition was carried as above. The solution after heating was extracted with 10 per cent aqueous sodium hydroxide. On acidification the extract gave an amorphous precipitate. The solid was separated into two

constituents by fractional crystallization from glacial acetic
acid. The less soluble constituent was the monobenzyl ether
of tetrachlorohydroquinone identical with the material produced
in the similar experiment with Azo-bis-diethylacetonitrile.
Samples from the two runs gave no mixed melting point depression
and had identical infrared spectra. The mother liquors from
the separation of the benzyl ether gave a material which was
amorphous but had an infrared spectrum identical with that of an
authentic sample. The spectrum showed no significant absorption
at 13.25 microns showing the absence of the monobenzyl ether.

The steam distillate from the reaction mixture was examined
for bibenzyl in the following manner. The last fraction from
the recrystallization of tetramethylsuccinonitrile was dried
and the infrared spectrum was determined in a Nujol mull. The
spectrum was identical to that of pure dinitrile and showed no
absorption at 13.25 microns (characteristic of all benzyl com-
pounds studied including bibenzyl). The steam distillation
residue gave tetrachlorohydroquinone di-(2-cyano-2-propyl) ether,
however, no m.p. $166-7^{o}$. The crude residue gave a spectrum
which had no absorption at 13.25 microns.

Decomposition of Azo-bis-isobutyronitrile in Chlorobenzene
containing Chloranil was carried out and the products were
worked up as described for other experiments. Yields are
summarized in Table I.

Attempted Syntheses of Tetrachlorohydroquinone Mono Benzyl
Ether. Several attempts were made to prepare this compound by

the alkylation of the hydroquinone with benzyl chloride. With
aqueous or alcoholic sodium hydroxide or with potassium carbo-
nate and dry acetone only unreacted hydroquinone and the diether
could be isolated. With sodium hydride in dry ether the start-
ing materials were recovered unchanged.

Preparation of tetrachlorohydroquinone dibenzyl ether.
Eight g. (0.03 mole) tetrachlorohydroquinone was added to 2.6 g.
(0.065 moles) sodium hydroxide in 100 ml. water. The solution
was heated to reflux and 9.0 g. (0.07 mole) benzyl chloride
was added dropwise. After the addition was complete the solution
was refluxed for two more hours. On cooling a precipitate formed
which was recrystallized from 95 per cent ethanol, m.p. 173.5-
173.8°. Anal. calc. for $C_{20}H_{14}O_2Cl_4$; C, 56.0; H, 3.28; Cl, 33.2;
found; C, 57.8; H, 3.47; Cl, 31.8.

Structure of Tetrachlorohydroquinone Monobenzylether. The
potentiometric titration of the substance in water solution
indicated an equivalence point at pH 8.4. The neutral equiva-
lent found was 332 as compared with the calculated value of
337. Since the compound could not be made easily by alkylation
the monoether was converted to the diether. A 0.5 g. sample of
the product from the decomposition of azo-bis-diethylacetonitrile
in toluene containing chloranil was dissolved in the minimum
volume of five per cent aqueous sodium hydroxide and heated to
reflux. The 0.2 ml. benzyl chloride was added dropwise and
the solution was refluxed for four hours. A solid separated
during the heating period and after cooling it was extracted

## TABLE I

### Decomposition of Azonitriles in the Presence of Chloranil

| Azonitrile | Moles Azonitrile X10² | Moles Chloranil X10² | Solvent (50 ml.) | Yields (moles x 10²) | | | R-R |
|---|---|---|---|---|---|---|---|
| | | | | $\overset{Cl\ Cl}{\underset{Cl\ Cl}{RO\text{-}OR}}$ | $\overset{Cl\ Cl}{\underset{Cl\ Cl}{HO\text{-}OR}}$ | $\overset{Cl\ Cl}{\underset{Cl\ Cl}{HO\text{-}OCH_2C_6H_5}}$ | |
| $Et_2C\text{-}N=NC\ Et_2$ (CN, CN) | 1.5 | None | toluene | | | | 1.09 |
| $Et_2C\text{-}N=NC\ Et_2$ (CN, CN) | 0.5 | 1.3 | toluene | 0.45 | | 0.08 | 0.31 |
| $Et_2C\text{-}N=NC\ Et_2$ (CN, CN) | 1.3 | 1.3 | Chloro-benzene | 0.67 | 0.66 | | 0.47 |
| $Me_2C\text{-}N=NC\ Me_2$ (CN, CN) | 1.0 | None | toluene | | | | 0.86 |
| $Me_2C\text{-}N=N\text{-}C\ Me_2$ (CN, CN) | 0.94 | 1.0 | toluene | 0.27 | 0.036 | 0.032 | 0.36 |
| $Me_2CN=NC\ Me_2$ (CN, CN) | 1.1 | 0.53 | Chloro-benzene | 0.29 | 0.037 | | 0.46 |

with other. The ether was evaporated and the solid residue was recrystallized from 95 per cent ethanol, m.p. 173-5° no depression on admixture with authentic material. The infrared spectrum was also identical with that of the authentic material.

Alkylation of tetrahydroquinone mono (3-cyano-3-pentyl) ether. The proof of structure of the monobenzyl ether by conversion to the dibenzyl ether involves the assumption that some other ether would not be cleaved and then dibenzylated under the reaction conditions. Since it is especially important to demonstrate that the substance was not the cyanoalkyl ether a small sample of the latter compound was benzylated under identical conditions. The white product was recrystallized from methanol and melted at 230-50° but depressed the melting point of authentic dibenzyl ether.

Decomposition of ω,ω'-azotoluene in Toluene containing Chloranil. A 2.46 g. (0.014 mole) sample of chloranil and 0.21 g. (0.001 mole) impure azo-bis-toluene were dissolved in 500 ml. toluene and heated to reflux for 48 hours. After cooling, the solution was extracted with 10 per cent sodium hydroxide until the extracts were clear. Acidification of the aqueous extract with dilute sulfuric acid gave 0.29 g. (0.0009 mole) of mono-benzyl ether which after recrystallization from glacial acetic acid melted at 139-40°. No products could be isolated from the tarry residue from steam distillation of the oil phase from the extraction.

Determination of Ketones. The determinations were carried out by a variation of the method of Siggia (8). An aliquot of

(8) Siggia, "Quantitative Analysis via Functional Groups", John Wiley and Sons, Inc., New York (1949); p. 17.

the test solution was pipetted into 50 ml. of a hydroxylamine hydrochloride solution (35 g. in 160 ml. distilled water diluted to one liter with 95 per cent ethanol). The liberated hydrochloric acid was titrated potentiometrically with either 0.2 or 0.5 N standard aqueous sodium hydroxide. The precision of the determination, evaluated by synthetic mixtures, was $\pm$ 5 per cent.

For those samples which contained both acetone and acetophenone the total ketone and acetone contents were determined in separate samples. For the latter the sample was pipetted into a special distilling flask equipped with a long right angle side arm containing a condenser in the vertical portion. Ten ml. benzene (Baker and Adamson, thiophene free, reagent grade) was added as a carrier. The acetone and benzene were then distilled over a water bath into 50 ml. hydroxylamine hydrochloride solution. This solution was then titrated as described above.

Determination of Alcohols. Methyl lithium (9) dissolved in

(9) H. Gilman, Zoellner and Selby, J. Am. Chem. Soc., 55, 1252 (1933).

in di-n-butyl ether, was first equilibrated in a flask equipped with a magnetic stirrer and connected to a gas buret, until the volume of gas no longer varied (2-3 hours). After equilibration,

one or two ml. of the sample was injected through a rubber
nipple by means of a hypodermic syringe. The solution was
stirred and the volume was measured after variation caused
by the heat of the reaction had ceased. A blank of 0.87 ml.
for each ml. of solution was determined empirically and was sub-
tracted from each determination. The precision was ± 10 per
cent.

Decomposition of Peroxides. The peroxide was weighed in
a 50 ml. volumetric flask (approximately 20 millimoles per
50 ml.) and diluted to the mark with cumene. Mixtures of
di-tert-butyl peroxide and di-$\alpha$-cumyl peroxide were prepared
by dissolving approximately 20 millimoles di-tert-butyl perox-
ide and a calculated amount of the cumyl peroxide in 50 ml.
The amount was calculated to give approximately equal concentra-
tions of cumyloxy and tert-butoxy radicals at the beginning of
the run. The calculations were based upon reported first order
rate constants[10,11]. The peroxide sample to be decomposed was

(10) Raley, Rust and Vaughan, ibid., 70, 88, 95 (1948).

(11) Kharasch, Fono and Nudenberg, J. Org. Chem. 16, 105 (1950).

pipetted from the volumetric flask into a round bottomed, long-
necked flask with a constriction in the neck. The flask was
chilled in an ice bath and evacuated with a Cenco Hyvac pump.
The flask was sealed at the constriction while still evacuated
and allowed to come to room temperature. The flask was then
immersed in a thermostated oil bath (132.5 ± 0.2°) for a period

calculated to give more than 99 per cent completion[12]. From the

(12)   It was assumed that triphenylmethyl-tert-butyl peroxide
       decomposed at a rate comparable to that of di-tert-butyl
       peroxide.

decomposition residues bi-∝- cumyl, m.p. 117-8°, was isolated.

The decomposition of triphenylmethyl tert-butyl peroxide
always gave a yellow solution.  From the residue, besides bi-∝-
cumyl, an impure white solid, m.p. 164-6°, was isolated.  The
infrared spectrum was similar to that of triphenyl carbinol and
is believed to contain benzpinacol-diphenyl ether.

The solutions were analyzed for ketones and alcohol as
described above.  The results are summarized in Table II.

## TABLE II

Decomposition of Di-tert-alkyl Peroxides (ROOR') in Cumene at 172°.

| Run | R | R' | Moles Peroxide $\times 10^3$ | Moles Ketone $\times 10^3$ | Moles Alcohol $\times 10^3$ | Per Cent Ketone | Per Cent Alcohol |
|---|---|---|---|---|---|---|---|
| 1 | t-Bu | t-Bu | 20.47 | 7.25 | 31.25 | 17.7 | 74.5 |
| 2 | t-Bu | t-Bu | 24.00 | 8.10 | | 16.9 | |
| 3 | $\phi_3 C$ | t-Bu | 16.80 | 3.19 | 30.0 | 19.0 | 89.5 |
| 4 | $\phi C(CH_3)_2$ | $\phi C(CH_3)_2$ | 0.148 | 0.247 | | 81 | |
| 5 | t-Bu $\phi C(CH_3)_2$ | t-Bu $\phi C(CH_3)_2$ | 24.91 0.0819 | 10.30[b] | 43.8 | 19.8 | 87.5 |
| 6 | t-Bu $\phi C(CH_3)_2$ | t-Bu $\phi C(CH_3)_2$ | 28.15 0.0912 | 9.96[c] | 48.8 | 17.8 | 84 |
| 7 | t-Bu $\phi C(CH_3)_2$ | t-Bu $\phi C(CH_3)_2$ | 24.3 0.099 | 10.58[b] | | 21.8 | |
| 8 | t-Bu t-Bu | t-Bu $\phi_3 C$ | 22.42 20.05 | 15.20 | 59.09 | 23.4[a] | 69.5 |
| 9 | t-Bu t-Bu | t-Bu $\phi_3 C$ | 25.59 5.343 | 11.58 | 46.52 | 20.3 | 75.0 |

a. Ketone yield calculated on basis of t-butoxy radical.

b. Total ketone.

c. Acetone only.

## TABLE III

Apparent Rates of AIBN Decomposition Measured by DPH

Disappearance in Carbon Tetrachloride

| Run | $[DPH]_o \times 10^3$ (m./l.) | $[AIBN]_o \times 10^2$ (m./l.) | T | $t_c$ (min) | $k_1 \times 10^6$ sec.$^{-1}$ |
|---|---|---|---|---|---|
| 43 | 0.278 | 2.640 | 60 | 27 | 3.25 |
| 44 | .278 | 3.96 | 60 | 18.5 | 3.17 |
| 45 | .511 | 3.961 | 60 | 29 | 3.71 |
| 46 | .128 | 1.321 | 60 | 22 | 3.67 |
| 51 | .128 | 1.309 | 60 | 25 | 3.32 |
| 54 | .0639 | 0.639 | 60 | 22 | 3.49 |
| 56 | .0639 | .346 | 60 | 42.6 | 3.61 |
| 57 | .0639 | .419 | 60 | 29.5 | 3.47 |
| 62 | .630 | 4.854 | 40 | | 10.54[1] |
| 102 | .0773 | .492 | 62.5 | 31.5 | 4.16 |
| 100 | .124 | .656 | 62.5 | 34 | 4.6 |
| 103 | .0773 | .492 | 62.5 | 43.5 | 3.09[2] |
| 81B | | 5.23 | 62.5 | | 11.8[1] |

1. Rate of decomposition by nitrogen evolution.

2. Sealed tubs.

## TABLE IV

Apparent Rates of AIBN Decomposition Measured by

DPH Disappearance in Chlorobenzene

| Run | T | $(DPH)_0 \times 10^3$ (m/l) | $(AIBN)_0 \times 10^2$ (m/l) | $t_c$ (min) | $k_1 \times 10^6$ |
|-----|------|------|------|------|------|
| 68 | 60 | 0.143 | 0.649 | 27 | 6.82 |
| 69 | 60 | 0.0717 | .325 | 26 | 7.08 |
| 70 | 60 | 0.0717 | .195 | 40.5 | 7.57 |
| 71 | 60 | 0.0717 | .455 | 25.25 | 6.83 |
| 72 | 62.5 | 0.0717 | .195 | 30 | 10.2 |
| 76 | 62.5 | 0.0717 | .257 | 23.5 | 9.79 |
| 71B | 62.5 | | 15.20 | | 15.4[1] |
| 97 | 62.5 | .133 | .615 | 27.5 | 6.54[2] |
| 106 | 74.4 | .0665 | .0661 | 29.25 | 28.67 |
| 83B | 74.4 | | 15.20 | | 78[1] |

1. Rate of decomposition by nitrogen evolution.
2. Sealed tube.

<u>Triphenylmethyl</u>. The triphenylmethyl was prepared from triphenylcarbinol via triphenylchloromethane. The carbinol was carefully purified, the steam distilled residue being recrystallized several times from ethanol. The triphenylchloromethane was made according to the Organic Synthesis procedure[13]. The

13. Organic Synthesis, vol. 23, p. 100.

triphenylmethyl radical was then generated by vigorously stirring the benzene solution of the chloride with mercury under a nitrogen atmosphere. The benzene used was the constant boiling portion of thiophene free benzene distilled through columns of ten theoretical plates or better and subsequently dried over sodium.

For the reactions in which the triphenylmethyl solution was used directly, the solutions were analyzed either by the benzoyl peroxide method,[14] or by the oxygen absorption method.[15]

14. G. S. Hammond, A. Ravve, F. J. Modic, <u>Anal</u>. <u>Chem</u>. <u>24</u>, 1373, (1952).

15. M. Gomberg, <u>Ber</u>. <u>33</u>, 3150, <u>Ber</u> <u>37</u>, 3538-47.

Because of personal preferance, the latter was used exclusively in the study of all the reactions of trityl. The earlier runs were made in a non thermostated absorption apparatus and therefore are not as accurate as some of the later determinations.

Crystalline hexaphenylethane was sought after in various ways. An apparatus similar to Gomberg's[16] was constructed, but

16. M. Gomberg and Cone <u>Ber</u>. <u>37</u>, 2033-51.

for some reason the triphenylmethyl could not be crystallized
satisfactorily.  Yellow solids containing relatively large amounts
of peroxide were the only products obtainable.  A dry box
flushed with Argon was tried, but with little success.  Apparently
a complete exclusion of oxygen is extremely difficult.  Finally,
a high vacuum system was constructed.  Recrystallization was
tried by distilling solvents from one part of the system to
another, and filtration was conducted by creating unequal pres-
sures within the system by means of solvent reservoirs and stop-
cocks.  Even though care was taken to thoroughly evacuate the
system initially and to use solvents distilled under inert
gases, it was found that the longer and more numerous the opera-
tions the more impure the product obtained.  The best result
obtained was a three day procedure in which the solid residue
left after evaporating off the benzene was washed with acetone.
This resulted in a white solid which gradually turned yellow
while still in the system.  Analysis showed that 90.2% of the
weight was radical.  This does not take into account the
absorption of oxygen by the solid during weighing and trans-
ferring.  This absorption was found to proceed such that about
20% of one solid sample became converted to oxygenated products
in a three hour period.  Since hexaphenylethane was still this
labile in the crystalline form, further experiments along these
lines were discontinued.  It was hoped at the time these experi-
ments were started that perhaps it might be possible to stockpile
large quantities of pure hexaphenylethane.

<u>Triphenyl-Methyl Quench.</u> (a) A benzene solution of tri-
phenylmethyl which had been prepared, but not used for a month
or so was quenched with methanol, iodine and pyridine. The
methanol and pyridine were added in slight excess. The super-
natant liquid was then washed with approximately 20 cc of
distilled water followed by three 20 cc portions of thiosulfate
solution. The benzene layer was then dried under vacuum and the
residue chromatographed. 1.0561 grams of triphenylmethane and
.3402 grams of p-benzhydryltetraphenylmethane were recovered.
A total of 2.8160 grams were recovered over a range of 118
fractions. The fact that products dribbled out over a wide
range of eluents suggests that a number of different compounds
existed in the mixture.

(b) A freshly prepared benzene solution of triphenylmethyl
was quenched. A relatively large amount of triphenylmethyl
ethyl ether was recovered. However, a surprising amount of
p-benzhydryltraphenylmethane was isolated as well as triphenyl-
carbinol in somewhat lesser amounts. Although 203 fractions
were taken, the above three compounds seem to predominate.

(c) A freshly prepared benzene solution of triphenylmethyl
was quenched with N-acetylethanolamine, but only oily and
colored products resulted.

(d) Triphenylmethyl solutions react with oxygen as described
by Gomberg.[17] That the reaction gives side products besides the

17. M. Gomberg, <u>Ber.</u> <u>37</u>, 3538-47.

main product of detritylperoxide has been confirmed. The solution slowly decomposing in the dry box in the presence of a very small amount of oxygen gave more side products than the exposure to atmospheric conditions. Gomberg states that the reaction of trityl with gaseous oxygen is complete in two minutes. However, it was found for a trityl and nitrosobenzene reaction mixture that 12 minutes are required for a maximum oxygen absorption even with vigorous stirring.

Nitrobenzene. (a) Equal molar quantities of nitrobenzene and triphenylmethyl were mixed. After two months, the solution still absorbed oxygen. Before the reaction mixture could be worked up, several more months elapsed and the benzene had diffused out through the rubber stopper and stopple. The solid residue was taken up with acetone which left a solid residue whose melting point corresponded to that of peroxide. The acetone was then evaporated off and the residue steam distilled. A total of 0.165 grams of nitrobenzene was recovered as compared to 0.196 grams of nitrobenzene originally introduced. Of the total products recovered, the identified portions were ditritylperoxide, 0.1562 grams (6.5% of total), nitrobenzene 0.165 grams (6.9%), triphenylmethane 0.6526 grams (27.2%), p-benzhydryltetraphenylmethane .2409 grams (10%), and triphenylcarbinol 0.8680 grams (36.4%).

(b) Nitrobenzene was distilled into a flask containing solid hexaphenylethane in vacuum rack. The nitrobenzene was

removed by distillation under vacuum at room temperature. After
10 days, when only solid residue remained, the flask was taken
off of rack and a portion of the sticky solid analyzed by oxygen
absorption. It was found that 27.2% of weight was still radical.
When flask with solid was allowed to stand exposed to the atmos-
phere, the solid which was originally a light yellow color turned
to a dark brown and finally to black. This black tar was dissolved
in acetone and transferred to an Erlenmeyer flack. Peroxide was
filtered off. At this point peroxide continued to form and was
also removed by filtration. Total peroxide recovered .2394
grams. Of the chromatographic fractions the following were
identified: triphenylmethane 0.2053 grams, p-benzhydryltetra-
phenylmethane 0.2088 grams, and triphenylcarbinol .8796 grams.
The unidentified fractions total another .3785 grams.

(c) Nitrobenzene and triphenylmethyl were mixed in the
vacuum rack under conditions similar to that used in (b). This
time the mixture was allowed to stand under vacuum for thirty
days. The main quantity of nitrobenzene came off in about
six days. After that time a more or less constant small amount
collected in the trap every day. This small amount was still
collecting at the end of the thirty day period when the vacuum
system was accidentally broken. The solid residue was yellow
and quite hard. A sample was obtained for analysis by drilling
a hole in the solid with a spatula. This was so that a repre-
sentative sample, not just the solid occuring on the surface,

could be obtained. On oxygenation 32.4% of the weight of the
sample was found to be apparent triphenylmethyl. After one
day the solid acquired an orange color on its surface. After
three days, analysis showed only 18.5% triphenylmethyl activity.
The surface had become somewhat sticky, but the interior
portions were still a dry yellow solid.

The mixture was then taken up in about 100 cc of acetone
and the insoluble material filtered off. This was assumed to
be the peroxide, but may have contained some p-benzhydryltetra-
phenylmethane. This acetone insoluble part weighed 2.5367
grams. In filtration, some of the filtrate was accidentally
spilled so that the remainder of the products could only be
determined in a relative manner. After stripping off the
acetone from the filtrate, the residue was vacuum distilled
using a temperature of 80 to 85°. Nitrobenzene was obtained.
The weight after removal of a sample for refractive index
determination was 0.632 g. Chromatography of the residue on
alumina yielded triphenylmethane, 0.3696 grams (19% of products
recovered), and p-benzhydrytetraphenylmethane, 0.2357 grams (12%).
Fractions corresponding to approximately 30% of the products
recovered appear to be triphenylcarbinol although characteri-
zation has not been completed. A total of 18 per cent of the
acetone soluble solid was obtained in identifiable fractions.

Nitrosobenzene. Nitrosobenzene was prepared using directions
found in Organic Synthesis.[18] Purification was carried out by

18. Organic Synthesis, Vol. 25, 80.

recrystallizing from alcohol or by subliming. Better looking
material was obtained by sublimation.

A reaction was carried out using equimolar quantities of
nitrosobenzene and triphenylmethyl. Trityl activity declined
fairly rapidly at first, but then leveled off. The reaction
mixture still absorbed some oxygen after two weeks. Products
identified from the various oxygenated fractions were
azoxybenzene, p-benzhydryltetraphenylmethane, triphenylcarbinol,
triphenylmethane, and possibly tetraphenylmethane. The main
reaction was set aside and lost in the period of interest in
other fields.

The appearance of azoxybenzene from this reaction mixture
is not surprising since a study of the thermal decomposition
products of nitrosobenzene shows that a large portion of the
products formed is azoxybenzene. A sample of nitrosobenzene
which had stood in an open bottle in the lab for some time had
turned to a dark black tarry oil. This was poured on several
inches of alumina and successively eluted with solvents of
greater polarity ranging from Skellysolve B to benzene. Of the
total solids obtained, 70 percent was found to be azoxybenzene.

Trinitrobenzene. An excess of Eastman white label tri-
nitro benzene was mixed with triphenylmethyl in benzene. The
trityl activity decreased very rapidly at first, but it is
difficult to say whether this was due to a reaction or to an
inadvertant inclusion of air into the reaction flask. After the
initial decrease the activity remained fairly constant. The
reaction is currently being worked up for products so the results

are far from conclusive. However, it appears that triphenyl-methane is obtained in smaller quantities than in the nitrobenzene reactions and that p-benzhydryltetraphenylmethane is missing. Triphenylcarbinol is obtained, but the relative quantity is undetermined.

## Reaction of Ditriphenylmethyl Peroxide With Sulfuric Acids.

The ditritylperoxide was obtained by air oxidizing benzene solutions of triphenylmethyl. This crude product was recrystal-lized by dissolving in boiling dioxane to the extent of .7 gm. per 100 cc of solvent and immediately ceasing further heating. The solution on standing overnite gave the crystals desired.

After the recrystallized peroxide was dried in a vacuum dessicator, 1.5798 gms. were weighed out. About 25 cc of concentrated $H_2SO_4$ was then added. A dark black mixture was obtained which did not noticeably turn warm. After 10 minutes, crystals were still floating around in the sulfuric acid. After about a half an hour, a homogeneous solution appeared to have resulted so the mixture was poured on 500 cc of chopped ice. The light brown solid was filtered on a Beuchner and sucked free of excess water. The solid was then dissolved in ether, the ether dissolving all but a small amount of colored residue on the filter paper. The ether solution was washed with two portions of dilute KOH, the first portion giving a brown colored aqueous phase and the second portion a relatively clear aqueous layer indicating that the separation was essentially complete.

On acidification of the base solution, the color changed to a
light straw color.  This acidified solution was extracted with
ether.  On the third extraction, the ether was colorless although
the aqueous solution was still slightly colored.  This aqueous
solution would not decolorize bromine water.  The ether fractions
were dried with calcium chloride and evaporated down to about
50 cc.  The neutral fraction was further evaporated to about
20 cc and Skelly A added.  No precipitate formed as Gomberg[19]

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19.  Gomberg, Ibid.

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reported.  However on standing for two days, beautiful rhomboidal
crystals formed.  These were filtered and weighed.  Weight .7070 gms.
On drying in vacuum dessicator overnight, there was no weight loss.
A second and third crop of crystals were obtained weighing .2777
and .4040 gms. respectively.  The residue after evaporating off
the mother liquor weighed .1133 gms.   The residue of the base
soluble fraction weighed .0908 gms.  These fractions represent
a total 1.5528 gms. of recovered products from the 1.5798 gms.
of peroxide originally reacted.

Benzophenone was searched for in the mother liquor residue
by washing with $CCl_4$ and taking infra red spectra of the $CCl_4$
solution.  The excess $\phi_3COH$ was not very soluble in $CCl_4$.  Attempts
were made to make carbonyl derivatives (oxime, semicarbazone)
from synthetic mixtures but were not uniformly successful.
Attempts to separate a synthetic mixture by chromatography also
failed, at least in its quantitative aspects.

The base soluble portion was found to absorb bromine with evolution of HBr. However, efforts to sublime phenol failed even though in synthetic mixtures containing phenol, the phenol could readily be separated by sublimation techniques. This residue was then dissolved in acetone and evaporated on a salt plate in order to obtain infra-red spectrum.

## RESULTS

The yield of triphenylcarbinol in this experiment was 86.7% of actual weighed material. Estimates run the yield up as high as 91% basing the calculations on 2 moles of $\emptyset_3COH$ as being theoretically obtainable from each mole of peroxide.

Benzophenone was found in the mother liquor. Although neither the compound nor its derivative could be isolated, an estimate of .0136 gms. was made by applying Beer's law to the carbonyl frequency of the infra-red spectrum. The estimate of 91% for the triphenylcarbinol is obtained by assuming that what is not benzophenone is the neutral fraction is triphenyl-carbinol.

Phenol could not be isolated although its absence should not be inferred from this failure. The residue was dried by placing in a vacuum dessicator and pumping on it overnight. The phenol if present, could well have sublimed off during this procedure. The interesting observation is that there is some phenolic substance present which is not the simple phenol. This was shown by the non-sublimable solid absorbing bromine

with evolution of HBr. The I. R. shows that there might also be some sulfonated product present in this acidic fraction. The $\phi_3$C-grouping, if present at all, is certainly not a major constituent. All of the triphenylmethyl type compounds, but one, in our collection show strong bands at $13.2\mu$ and $14.3-14.4\mu$. There is a questionable bump in the spectrum in question at 13.2 and one at 14.2.

Methacrylonitrile was washed with two percent aqueous sodium hydroxide and with water to remove the stabilizer. After drying over calcium chloride the monomer was distilled through an efficient column under nitrogen. Material boiling at 88.5-90°, $N_D^{25}$, 1.3980 was used for subsequent studies.

Polymerization Experiments. Solutions were prepared by dissolving weighed amounts of azo-bis-isobutyronitrile in methacrylonitrile. Samples were placed in constricted test tubes which had been carefully cleaned and dried. Each sample was degassed by freezing in a dry ice-acetone bath, evacuating and flushing with nitrogen, the entire procedure being repeated three times and the tubes were finally evacuated and sealed. The samples were heated in a thermostat at 62.5°. At intervals tubes were removed, cooled and opened. Polymer was precipitated by pouring the sample into methanol. The polymer was then reprecipitated twice by dissolving it in acetone and pouring it into methanol. Samples were then dried to constant weight.

Viscosity measurements were made with acetone solutions in an Ostwald viscometer having a flow time of 110 sec. at $25°$. Intrinsic viscosities $[N]$ were calculated from the relationship, $N_{sp}/C = N$, where C is the concentration of polymer in grams per 100 ml. The results reported in Table ___ were obtained by extrapolation to infinite dilution.

### TABLE V

Polymerization of Methacrylonitrile in bulk at $62-5°$

| Run | $[AIB]_0 \times 10^3$ moles/liter | $[AIB]^{\frac{1}{2}} \times 10^2$ | Polymerization Rate, in percent per hr. | N |
|-----|------|------|-------|------|
| 5 | 87.6 | 29.6 | 1.944 | 0.13 |
| 6 | 29.2 | 17.1 | 1.230 | 0.20 |
| 7 | 14.6 | 12.1 | 1.017 | 0.85 |
| 8 | 9.73 | 9.86 | 0.800 | 0.85 |
| 9 | 7.96 | 8.92 | 0.723 | 0.99 |
| 10 | 5.97 | 7.73 | 0.646 | --- |

Our work confirms previous reports (20) showing that the

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20. W. Kern and H. Fernow, J. Prakt. Chem. 160, 302 (1942).

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temperature interval $60-65°$ is convenient for the study of methacrylonitrile polymerization. The product obtained is white and granular and the polymerization rates at low conversions are proportional to the square root of the initiator concentration as is readily derived from the data in Table V.

## Discussion

These results will be treated in detail in forthcoming publications but the significant conclusions or indications will be pointed out at this time.
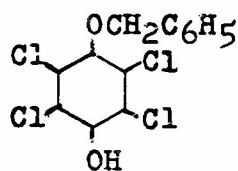
A major emphasis has been placed upon the study of "cage effects" in thermal decomposition reactions. Such effects have been frequently suggested as being of importance in determining the fate of radical pairs produced in thermal decompositions and the concept has met with rather varying response. It has been our experience that much better understanding is achieved by referring to the phenomena by the more cumbersome but also more specific designation of <u>diffusion control of the fate of primary decomposition products</u>. The concept of diffusion control of reactions such as the recombination of reactive free radicals is commonly accepted and the "cage effect" can be no more nor less than the microscopic reverse of the former phenomenon. Using this as a guide we are able to draw up some rough criteria as to the probability of occurence of important cage effects in decomposition reactions. The reaction which is believed to be subject to diffusion control must necessarily be one whose rate is likely to be as fast or faster than diffusion rates in liquids. This criterion may furthermore be modified somewhat to take account of dipole-dipole attraction which may operate in such a way as to prolong contact between primary products which have large dipoles (such as cyanoalkyl and acyloxy
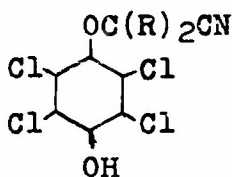
radicals), especially when they are produced in media with low
dielectric constants.

In a reinvestigation of the decomposition of di-tert-alkyl
peroxides we have failed to confirm the conclusions of Kharasch
and coworkers ( 5 ) that the fate of a given alkoxy radical
is influenced strongly by the identity of the parent peroxide.
Variations in the ketone/alcohol ratio (Table I) may occur
but are small enough to tax our analytical method.  The chosen
method of analysis is designed to be much more accurate than
that employed by the earlier workers and was carefully tested
for accuracy and precision.  Since we have neither confirmed
the results in the literature nor established that no variations
occur it will be necessary to defer final judgement (and
publication) until further investigations can be completed.  At
the present time we feel that there is no unequivocal evidence
for proximity effects in the decomposition of dialkyl peroxides
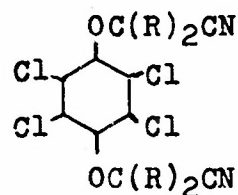in cumene.

The study of the scavenging of primary products of the
decomposition of bis-azonitriles by chloranil turned up a very
interesting phenomenon which was apparently missed completely
by Bickel and Waters ( 2 ).  This is the fact that in toluene
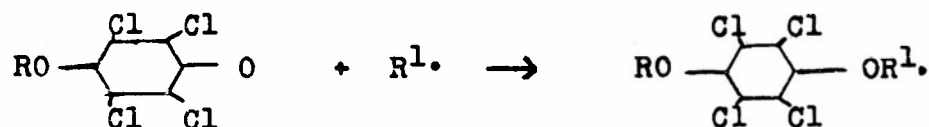solution the following compounds are produced from chloranil.



I $\qquad$ II $\qquad$ III

Compound III is the only diether found after an exhaustive search
and we are convinced that the unsymmetrical diether and the
dibenzyl ether were not produced in significant amounts. This
observation is difficult to reconcile with the rather obvious
mechanism for diether formation shown by equation (1). This

$$RO-\underset{\underset{Cl\quad Cl}{}}{\overset{\overset{Cl\quad Cl}{}}{\bigcirc}}-O \quad + \quad R^1\cdot \quad \longrightarrow \quad RO-\underset{\underset{Cl\quad Cl}{}}{\overset{\overset{Cl\quad Cl}{}}{\bigcirc}}-OR^1\cdot$$

would require that the semiquinone radical with a benzyl group
attached to oxygen have a very different relative reactivity
in hydrogen abstraction and radical coupling reactions than
the semiquinone in which R is the cyanoalkyl group. Two
explanations have been considered. The first is that two
cyanoalkyl radicals produced in the thermal decomposition
become attached to chloranil before they have been separated
by diffusion. The second, which is suggested by other work in
these laboratories, is that the diether is formed, not by the
attack of a radical on a semiquinone but by the reaction of a
radical with a molecular complex of chloranil with a radical.
We hope that more study can be devoted to the problem but
intend to publish the completed results shortly.

The very careful reinvestigation of the system nitro-
benzene-triphenylmethyl has shown that the previously reported
oxidation of triphenylmethyl by nitrobenzene can not be repeated.
We can only conclude that Dr. Raave's early work was misleading
either because of the spurious inclusion of unknown catalytic

materials or because of his inaccurate observation of experimental results.

The study of methacrylonitrile polymerization was initiated with the intention of comparing the chain transfer activity of growing radical chains with that of analogous tertiary cyanoalkyl radicals produced in the decomposition of azonitriles. Since the data for the latter is available (see accompanying manuscript) for butyl mercaptan as a transfer agent, it is anticipated that Dr. Sen will be able to complete the study within the next few months as he will continue the work for a short time with support from another source.

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